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# Canadian Journal of Research

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NUMBER 6

## A THEORY OF THE SIZE DISTRIBUTION OF PARTICLES IN A COMMUNUTED SYSTEM<sup>1</sup>

BY LAURENCE GRIFFITH<sup>2</sup>

### Abstract

It is shown that the problem of the size distribution of particles in a system that has been ground can be treated by the general methods of the theory of probability. The mathematical procedure employed is almost identical in form with that used in the classical statistical mechanics of gases, although the fundamental ideas are different, as the molecules of a solid are not free to move. The distribution laws developed agree with the known empirical laws for particles of sizes down to about one micron, but proof of the theory will depend upon study of size distributions in colloidal systems.

Three empirical laws concerning the size distribution of particles in a comminuted system are in common use:

1. Size distributions often give fairly straight lines on logarithmic-probability paper (1):

$$Y = A + M \log x, \quad (1)$$

where  $Y$  is the cumulative per cent of material finer than the size  $x$ , on a scale whose intervals are based upon values of the probability integral, and  $A$  and  $M$  are constants.

2. Gaudin's law (4), which in the convenient form deduced by Schuhmann (7), is

$$y = 100 \left( \frac{x}{R} \right)^m, \quad (2)$$

where  $y$  is the cumulative per cent of material finer than the size  $x$ , and  $R$  and  $m$  are constants.

3. The Rosin-Rammler equation (2, 5)

$$r = 100e^{-(\frac{x}{k})^m}, \quad (3)$$

where  $r$  is the cumulative per cent of material coarser than size  $x$ ,  $e$  is the base of natural logarithms, and  $m$  and  $k$  are constants.

Schuhmann has shown that Equations (2) and (3) approach each other asymptotically as  $x$  is reduced.

There is no obvious relation between the first two of these laws, and since they give very different results when used to extrapolate experimental results

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into the region corresponding to the very fine sizes, it is obvious that such an extrapolation cannot be done with any feeling of certainty. This report is a theoretical deduction of an equation for size distribution: the expression found is one of the particular integrals of the differential probability equation and as such is consistent with the first of the above laws; it is also in excellent agreement with Gaudin's law, becoming identical with it when applied to particles of the larger sizes.

### Fundamental Considerations

The comminuted system, which is assumed to be homogeneous, is considered as divided into a sheaf of elementary systems, according to the size of the particles. Thus the elementary system  $n$  will contain all those particles whose (average) diameter is between  $x_n$  and  $x_n + \Delta x$  centimetres, the class interval  $\Delta x$  being constant. The surface energy of a molecule in this elementary system, owing to its location in a particle of this size, will be taken as  $E_n$  and the number of molecules in it taken as  $N_n$ . The numbers  $N_0, N_1, N_2, \dots, N_n, \dots$  thus constitute the law of the partition of (surface) energy in the total system and define its macro-state.

The following relations must also hold

$$N_0 + N_1 + N_2 + \dots + N_n + \dots = N,$$

where  $N$  is the total number of molecules in the system and is fixed;

$$N_0 E_0 + N_1 E_1 + N_2 E_2 + \dots + N_n E_n + \dots = E,$$

where  $E$  is surface energy of the system, i.e., the increase of energy on comminuting the system, the temperature, pressure, chemical state, and state of strain being the same finally as initially.

The number of ways in which such a size distribution can occur is easily determined; the value so obtained will be termed the statistical weight of the size distribution and will be designated by the letter  $G$ . The number of ways in which the  $N_0$  molecules in the 0th elementary system could be chosen from all the  $N$  molecules is

$$\frac{N!}{N_0!(N - N_0)!}$$

This system having been completed, the next elementary system is filled with  $N_1$  molecules, having  $(N - N_0)$  molecules from which to choose, giving the number

$$\frac{(N - N_0)!}{N_1!(N - N_0 - N_1)!}$$

and so on. The number of ways in which all the elementary systems could be filled will then be the product of all the number of ways for the individual elementary systems, and this number might be taken as the value of  $G$  for the size distribution. However, there is an immediate objection to this method of determining  $G$  in that the condition of rigidity has been violated. This objection can readily be overcome if it be assumed that the individual molecules do not possess identity; this is equivalent to dividing the above

number by the number of permutations of  $N$  things, taken  $N$  at a time, i.e.  $N!$  The value of  $G$  is therefore taken as

$$G = \frac{1}{N_0! \cdot N_1! \cdot N_2! \cdot \dots \cdot N_n! \cdot \dots} \quad (4)$$

### The Basic Postulate and the Resulting Distribution Law

As a primary postulate it is assumed that the size distribution that occurs naturally is that for which  $G$  is a maximum.

This condition is readily determined (6) when it is assumed that any particle has just as good a chance of being broken as any other.

$$w_n = ae^{-BE_n}, \quad (5)$$

where

$$w_n = \frac{N_n}{N},$$

and  $e$  is the base of natural logarithms.

The constants  $a$  and  $B$  are both positive;  $a$  is given by

$$\frac{1}{a} = \sum e^{-BE_n},$$

whence

$$w_n = \frac{e^{-BE_n}}{\sum e^{-BE_n}}. \quad (6)$$

$B$  can be obtained from

$$\frac{\sum E_n e^{-BE_n}}{\sum e^{-BE_n}} = \frac{E}{N}. \quad (7)$$

### The Value of $E_n$

The energy  $E$  given to the system was absorbed in the production of new surface;  $E_n$  is thus the energy of each of the  $N_n$  molecules in the  $n$ th elementary system, due to the surface in this system. If the particles are cubes, the surface area of one of them is  $6x_n^2$ . If the surface energy  $g$  is assumed to be independent of the size of a particle then the energy of this particle is  $6x_n^2g$ .

But the number of molecules in this cube is  $\frac{x_n^3 D}{m}$ , where  $D$  is the density of the material constituting the system and  $m$  is the mass of one of its molecules. Therefore the energy per molecule is

$$E_n = \frac{6gm}{D} \cdot \frac{1}{x_n}. \quad (8)$$

### On the Parameter "B"

If by analogy with the kinetic theory of gases the equation

$$S = k \log G, \quad (9)$$

where  $S$  is the (surface) entropy, is introduced, then  $B$  could immediately be written as

$$B = \frac{1}{kT}, \quad (10)$$

where  $T$  is the absolute temperature and  $k$  is Boltzmann's constant. However, the primary postulate then asserts that a comminuted system is an equilibrium system. But if the system is put through a screen, that portion that will not pass through is no longer an equilibrium system and it could be asserted that Maxwell's demon had been raised. The possibility of finding a new method of determining the elusive quantity  $g$  makes the risk seem almost worth while.

### The Integral Form of the Distribution Law

The expression

$$w_n = a e^{-BE_n} \quad (5)$$

gives that fraction of the molecules (which is equal to that fraction of the weight of the system) that occurs in particles of sizes between  $x$  and  $x + \Delta x$ . The density of molecules, i.e., the number of molecules per unit of  $x$ , is

$$\frac{a}{\Delta x} \cdot e^{-BE_n}.$$

The fraction that occurs in any range  $\delta x$  is then

$$\delta w = \frac{a}{\Delta x} \cdot e^{-BE_n} \delta x.$$

Summing up for all the molecules

$$1 = \frac{a}{\Delta x} \sum e^{-BE_n} \delta x.$$

Therefore

$$\delta w = \frac{e^{-BE_n} \delta x}{\sum e^{-BE_n} \delta x}.$$

Allowing  $\delta x$  to become smaller and smaller, and substituting from Equation (8)

$$dw = \frac{e^{-\frac{aBgm}{Dx}} dx}{\int_0^M e^{-\frac{aBgm}{Dx}} dx}, \quad (11)$$

where  $M$  is the size of the largest particle occurring in the system.

The integral

$$\int_0^x dw \quad (12)$$

is the cumulative weight fraction of material having a size less than  $x$ . Multiplied by 100 it is the cumulative per cent of material having a size less than  $x$ . The latter is the form in which experimental results are easily expressed. Evaluation of Equation (12) requires the evaluation of

$$\begin{aligned} & \int_0^x e^{-\frac{aBgm}{D} \cdot \frac{1}{x}} dx \\ &= u \left\{ \left( \frac{x}{u} \right) - \log \left( \frac{x}{u} \right) - \frac{1}{1.2!} \left( \frac{u}{x} \right) + \frac{1}{2.3!} \left( \frac{u}{x} \right)^2 - \frac{1}{3.4!} \left( \frac{u}{x} \right)^3 + \dots \right\}, \quad (13) \end{aligned}$$



where

$$u = \frac{6Bgm}{D} \quad (14)$$

The series within the braces in Equation (13) can, by comparison with the series

$$e^{-\frac{u}{x}} = 1 - \frac{u}{x} + \frac{1}{2!} \frac{u^2}{x^2} - \frac{1}{3!} \frac{u^3}{x^3} \dots \dots \dots$$

be shown to be convergent for all finite values of  $\left(\frac{x}{u}\right)$ , including zero, and to approach the value zero as  $x$  approaches zero. Consequently the constant of integration is zero.

From Equation (13) it is seen that when  $x$  is large in comparison with  $u$ , the cumulative weight fraction finer than the size  $x$  is

$$\int_0^x dw = \frac{x}{M} \quad (15)$$

and the

$$\text{Cumulative weight per cent finer than } x = \frac{100x}{M} \quad (16)$$

#### Modifications Introduced by the Possibility of Selective Comminution

In calculating the probability of a given distribution it was implied that any particle had just as good a chance of being broken as any other, regardless of its size. The distribution law is based upon this implication. In many cases of comminution such an assumption is justified, but there are many others where there are a priori reasons to believe that particles of certain sizes are more likely to be crushed than others. The distribution law must therefore be generalized to include such cases. This can be done by again examining the manner in which the elementary systems were defined. The elementary system  $n$  was defined to contain all those particles whose diameter was between  $x_n$  and  $x_n + \Delta x$ ; i.e., one elementary system was introduced into the interval  $\Delta x$ . But there is no reason why only one elementary system should be placed in this interval, for  $\Delta x$  could be divided into  $p$  parts and an elementary system taken in each, so that the interval  $\Delta x$  would contain  $p$  elementary systems. In other words, its probability would be  $p$  instead of unity. The value of  $p$  for a particular region  $\Delta x$  may now be chosen to allow for the fact that certain size ranges may be specially protected, or specially attacked during the operation of comminution. Equation (6) becomes

$$w = \frac{p_n e^{-BE_n}}{\sum p_n e^{-BE_n}} \quad (17)$$

and Equation (11)

$$dw = \frac{p e^{-\frac{6Bgm}{D} \cdot \frac{1}{x}} dx}{\int_0^M p e^{-\frac{6Bgm}{D} \cdot \frac{1}{x}} dx} \quad (18)$$

Equation (18) is a distribution such that the resulting state obeys the primary postulate, while the introduction of the a priori probabilities  $p$  allows the possibility of the occurrence of several such states.

### *Second Postulate*

The manner in which the values of  $p$  are to be chosen is a matter of some difficulty. The following rule is postulated:

The a priori probability  $p$  for a particular class of particle shall be so chosen that it is inversely proportional to the probability that a particle of that class will be comminuted.

In deducing the law given in Equation (16) it was implied that all particles had an equal chance of being crushed. The value of  $p$  was therefore taken as unity or, for reasons that will be seen shortly, as  $\frac{k}{x^0}$ , where  $k$  is a constant. Consider now the case of a system that is mixed with water to a very thin pulp and ground in a ball mill. As two balls approach each other to form a zone of compression, the fluid between them is forced aside, dragging the particles with it. By Stokes' law the speed with which the particles will move relative to the fluid will be proportional to the square of their diameters; therefore the small particles will have a better chance of escaping from the compression zone. For the a priori probability there may therefore be set

$$p = \frac{k}{x^2},$$

where  $k$  is a constant. This value can be substituted in Equation (18) and the integration carried out to give the distribution law for this case.

When grinding is carried out in such a way that no particles have any better chances than any others of escaping a zone of compression, the value of  $p$  is given by

$$p = \frac{k}{x^0}. \quad (19)$$

When grinding is done in a very dilute pulp so that marked segregation takes place,

$$p = \frac{k}{x^2}. \quad (20)$$

In actual practice neither of these extremes may be realized but rather some intermediate case, which may be represented by

$$p = \frac{k}{x^r}, \quad (21)$$

where

$$0 < r < 2.$$

It is to be noticed that there is no assurance that  $r$  will be independent of  $x$ , although to assume this will be to make a fairly valid approximation.

### A More General Distribution Law

Substituting from Equation (21) into (18) and forming Integral (12) there results:

Cumulative weight fraction finer than  $x$

$$= \frac{\left\{ -\frac{1}{(r-1)} \cdot \frac{1}{x^{r-1}} + \frac{1}{r} \frac{u}{x^r} - \frac{1}{2!} \cdot \frac{1}{r+1} \frac{u^2}{x^{r+1}} \cdots \right\}}{\left\{ -\frac{1}{(r-1)} \frac{1}{M^{r-1}} + \frac{1}{r} \frac{u}{M^r} - \frac{1}{2!} \cdot \frac{1}{r+1} \cdot \frac{u^2}{M^{r+1}} \cdots \right\}} \quad (22)$$

Where  $x$  is large compared to  $u$  this simplifies to:

$$\text{Cumulative weight fraction finer than } x = \frac{x^m}{M^m}, \quad (23)$$

where

$$m = -r + 1 \quad (1 > m > 0). \quad (24)$$

Equation (23) is Schuhmann's law, from which Gaudin's law can easily be deduced.

### A Formal Method of Application to Experimental Results

The application of Equation (22) to experimental results would be a matter of extreme difficulty. The distribution law of which this is the integral is however of the form

$$y = y_0 x^{-r} e^{-\frac{u}{x}}. \quad (25)$$

This equation is a particular integral of the probability equation

$$dy = \frac{y(x+b)dx}{px^2 + qx + r},$$

when the discriminant of the expression  $px^2 + qx + r = 0$  is equal to one and the roots are real and equal. Consequently if the cumulative size distribution curve is drawn from the experimental results and the results are retabulated on an equal size interval basis, the value of  $y_0$ ,  $r$ , and  $u$  could be found by the method of moments, Shepherd's corrections being applied if the experimental results seem to warrant it (3). Equation (25) could therefore be drawn, integrated graphically, and the resulting cumulative curve compared with the experimental results.

It should be noticed that if the value of the constant  $B$  is near that indicated by Equation (10), the deviation of Equation (22) from Gaudin's law is very slight even for the particles as small as one micron. This is most readily seen by substituting in Equation (25), which is the differential form of Schuhmann's equation modified by the factor  $e^{-\frac{u}{x}}$ . It is only for the particles smaller than one micron that this factor begins to differ appreciably from unity.

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## THE ALKALOIDS OF FUMARIACEOUS PLANTS XXXVI. *CORYDALIS THALICTRIFOLIA* FRANCH. AND THE CONSTITUTION OF A NEW ALKALOID, THALICTRIFOLINE<sup>1</sup>

BY RICHARD H. F. MANSKE<sup>2</sup>

### Abstract

*Corydalis thalictrifolia* Franch. has yielded eight alkaloids, four of which, namely, protopine, stylophine, *l*-corypalmine, and adlumidine, are known bases. The remaining four, thalictrifoline (alkaloid F58) ( $C_{21}H_{23}O_4N$ ), and its dehydro-base, alkaloid F59 ( $C_{20}H_{23}O_4N$ ), and alkaloid F60 ( $C_{20}H_{21}O_3N$ ), are new. The constitution of thalictrifoline has been elucidated. It is corydaline in which the 9:10-methoxy-groups have been replaced by a methylenedioxy-group.

*Corydalis thalictrifolia* Franch. is a native of the Himalayas and is related botanically to a number of species already investigated by the author. The section *Eucorydalis* Prantl. has been subdivided into eight subsections. The present plant is the type genus of one of those (*Thalictrifoliae* Fedde) and is the first to be examined chemically.

In gross appearance it differs from all species already investigated in that the ultimate segments of the compound leaves are quite large and somewhat fleshy, and the stem is stout and brittle. It is a facultative biennial but does not survive the local winter climate.

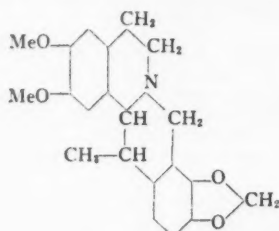
Chemical examination has disclosed the presence of eight alkaloids, only four of which, namely, protopine, stylophine, *l*-corypalmine, and adlumidine, are known bases. Of the remaining four, only two, thalictrifoline (F58), and its dehydro-base, have been adequately characterized. The others were obtained in amounts not adequate for positive characterization but are referred to as alkaloid F59 ( $C_{20}H_{23}O_4N$ ) and alkaloid F60 ( $C_{20}H_{21}O_3N$ ), in both cases the empirical formulae being questionable. Tetrahydropalmatine, so common in plants of subsection *Eucapnoides* Fedde, is definitely absent. Thalictrifoline is represented by  $C_{21}H_{23}O_4N$  containing two methoxyl groups. On oxidation with iodine in methanol it yields a dehydro-base, which, on reduction, forms an optically inactive isomer of the parent base. The quaternary base isolated as the chloride directly from the plant yields on reduction the same inactive alkaloid. This observation makes it probable that thalictrifoline has the structure of corydaline with two of the methoxyl groups

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replaced by a methylenedioxy group. Oxidation of the base with permanganate yielded *m*-hemipinic acid so that the given formula seemed to be the correct one. The oxidation products however did not include 3 : 4-methylenedioxy-phthalic acid (2), and in any event the presence of the methyl group in the assigned position required proof. Removal of the methylenedioxy group and methylation of the phenolic base yielded an alkaloid that was not identical with corydaline. This lack of identity is attributed to the fact that the asymmetric centres of thalictrifoline and of corydaline are not identical sterically. However, the base from thalictrifoline on oxidation and subsequent reduction yields *dl*-meso-corydaline identical with a specimen prepared from corydaline. The constitution of thalictrifoline is therefore that shown.



### Experimental

The material for the present investigation was grown in a local garden. After drying and grinding it weighed 5850 gm. of which the roots constituted 115 gm. During the methanol extraction of the latter a sparingly soluble salt, which proved to be potassium chloride, separated. Acetyl-ornithine was not present.

The procedure repeatedly used in the examination of other plants of this series was used throughout (1). The following is a summary:

Base hydrochlorides extracted from aqueous solution by means of chloroform:—

BC—Non-phenolic bases—thalictrifoline, stylophine, alkaloid F59, dehydro-thalictrifoline.  
BCE + EEC—Phenolic bases—*l*-corypalmine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform:—

BS—Non-phenolic bases—protopine, alkaloid F60.  
BSE + EES—Phenolic bases—not crystallized as base.

#### *Dehydro-thalictrifoline Hydrochloride*

The aqueous solution (SR) that was obtained by dissolving the chloroform extract from the acid solution was exhausted with ether, during which process a sparingly soluble salt separated. This was filtered off and recrystallized twice from hot water and then washed with methanol in which it is only

sparingly soluble. It then consisted of chocolate brown stout prisms that melted with effervescence at 271° C.\* The yield was about 1.2 gm.

That this was a quaternary salt was indicated by the fact that the addition of ammonia to its aqueous solution did not yield a precipitate. It was reduced to the tertiary base by boiling with zinc and dilute hydrochloric acid until the yellow colour had been discharged. The cooled solution was then basified with ammonia and extracted with ether. The somewhat concentrated ether extract deposited colourless rectangular plates of a base melting sharply at 151° C. It proved to be identical with *dl*-thalictrifoline obtained by racemisation of the natural base.

#### *Thalictrifoline (F58) and Its Constitution*

The fraction (BC) was redissolved in dilute hydrochloric acid, the filtered solution basified with ammonia, and extracted with a large volume of ether. The washed solution was evaporated, during which process a sparingly soluble base crystallized. It was first washed with ether and then recrystallized twice from hot methanol in which it is only sparingly soluble. As thus obtained thalictrifoline (yield, 7 gm.) consisted of colourless stout prisms melting sharply at 155° C.  $[\alpha]^{25} + 218^\circ$  ( $c = 0.4$  in methanol). It dissolves in sulphuric acid to yield an emerald green solution, which, when warmed, changed first to dark blue and then to brown. Calc. for  $C_{21}H_{23}O_4N$ : C, 71.39; H, 6.52; N, 3.97; 2 OMe, 17.56%. Found: C, 71.31, 71.48; H, 6.24, 6.59; N, 4.02, 4.22; OMe, 17.49, 17.50%.

#### *dl*-Thalictrifoline

A solution of thalictrifoline in hot ethanol containing an excess of sodium acetate was treated with iodine until the colour of the latter was permanent. The precipitated quaternary iodide was filtered off and boiled with zinc and dilute hydrochloric acid until the solution was colourless. An excess of ammonia was added and the liberated base extracted with ether. The somewhat concentrated extract deposited colourless crystals melting sharply at 151° C. either alone or in admixture with the base obtained from the dehydrothalictrifoline isolated directly from the plant. Calc. for  $C_{21}H_{23}O_4N$ : C, 71.39; H, 6.52; N, 3.97; 2 OMe, 17.56%. Found: C, 71.31, 71.48; H, 6.29, 6.42; N, 4.25, 4.24; OMe, 17.69, 17.89%.

#### *Oxidation of Thalictrifoline*

A solution of 1.5 gm. of the alkaloid in 250 cc. of water containing a few drops of hydrochloric acid was treated with sodium bicarbonate until the incipient turbidity was just permanent. An aqueous solution of permanganate was added until the colour was permanent for 30 min. The heated solution was decolorized with alcohol, filtered, evaporated to a small volume, acidified with hydrochloric acid, and exhausted with ether. The ether extract was redissolved in water, an excess of calcium acetate added, the filtered solution acidified with hydrochloric acid, and again exhausted with ether.

\* All melting points are corrected.



The residue from the ether crystallized readily. It was washed with a little ether; it then melted at 197° C. either alone or in admixture with a specimen of *m*-hemipinic acid. The *N*-ethyl-imide melted at 231° C. and in admixture with an authentic specimen it melted at 231 to 232° C. No success attended an exhaustive effort to isolate 3 : 4-methylenedioxy-phthalic acid from the more soluble fraction.

#### *Meso-corydaline from Thalictrifoline*

A solution of 1 gm. of thalictrifoline in 21 cc. of sulphuric acid and 25 cc. of water containing 2.5 gm. of phloroglucinol was heated to boiling for two minutes and then digested on the steam-bath for six hours (3). The cooled and filtered solution was neutralized with sodium bicarbonate and exhausted with ether. The residue from the ether extract was treated in methanol with an excess of diazomethane. After 24 hr. the solvents were removed and the residue was extracted with several portions of dilute hydrochloric acid. The filtered solution was extracted with ether, basified, and again extracted with ether. The washed extract on evaporation to a small volume yielded colourless crystals melting at 158° C. but in admixture with *meso*-corydaline the substance was completely liquid at 150° C. The base was therefore racemized by the usual process of oxidation and reduction. There was thus obtained a colourless resin, which, when seeded with a crystal of *meso*-corydaline, crystallized at once. It was washed with ether and with hexane; it then melted at 161° C. In admixture with a specimen of *meso*-corydaline melting at 163° C. it melted at 161 to 162° C.

#### *Alkaloid F59*

The ether filtrate from which the thalictrifoline had crystallized deposited a sparingly soluble base in the course of several days. It was recrystallized twice from chloroform-methanol, and it then consisted of very pale pink deep rectangular plates, which melted at 176° C., then largely solidified, and remelted at 192 to 200° C. This behaviour is reminiscent of bicuculline but a mixture of the two bases was completely liquid at 160° C. The yield was 1.8 gm. Alkaloid F59 dissolves in sulphuric acid to yield a colourless solution that slowly becomes emerald green; on heating, this changes to yellow-brown. Found: C, 70.28, 70.42, 70.26; H, 6.26, 6.58, 6.29; N, 4.16; OMe, 9.68, 10.56, 11.62, 9.58%. Calc. for  $C_{20}H_{23}O_4N$ : C, 70.38; H, 6.75; N, 4.10; 1 OMe, 9.09%.

#### *Stylophine*

The mother liquor from which alkaloid F59 had separated was neutralized with hydrobromic acid and the free base regenerated from the sparingly soluble salt thus obtained. It was recrystallized from chloroform-methanol, and it then consisted of colourless fine needles melting at 202° C. In admixture with a specimen of *l*-stylophine (m.p. 206° C.) it was completely liquid only at 200° C. That it consisted of a partly racemic *d*-stylophine was indicated by the low optical activity (+93°). It was racemized by oxidation with iodine and subsequent reduction, and it then melted at 220° C. either alone or in



admixture with an authentic specimen of *dl*-stylopine. The yield was about 0.1 gm.

#### *Adlumidine*

The ultimate mother liquor from which none of the above bases could be crystallized was dissolved in aqueous oxalic acid and the solution exhausted with ether. An excess of sodium hydroxide was added, and the bases were then extracted with ether. The residue from the washed extract was dried and left in contact with a little methanol. The mixture of crystalline bases that separated in the course of several days was filtered off and dissolved in hot chloroform. The solvent was evaporated and the resin dissolved in methanol. The base, which crystallized almost at once, was recrystallized from chloroform-methanol; it then consisted of colourless stout polyhedra melting at 238° C. In admixture with adlumidine it melted at the same temperature. The mother liquor from the first recrystallization yielded a small amount of protopine.

#### *Protopine*

The fraction (BS) was dried, dissolved in chloroform, and the filtered solution evaporated to dryness. The residue was dissolved in hot dilute hydrochloric acid and the salt that separated was proved to be protopine hydrochloride by conversion to the free base (m.p. 211° C.) The filtrate from the hydrochloride was basified with ammonia and extracted with ether. The washed extract was evaporated to dryness and dissolved in methanol. The base, which then crystallized, was slightly impure protopine (m.p. 206°). The total yield was about 2.5 gm.

#### *Alkaloid F60*

The methanolic solution from which no more protopine could be crystallized was neutralized with hydrogen bromide in methanol. A sparingly soluble salt was then obtained. The free base was regenerated from this and recrystallized from a small volume of methanol in which it is moderately soluble. It then melted at 92° C. with effervescence, presumably owing to loss of solvent of crystallization. A portion dried at 80° C. for 16 hr. melted at 123° C. The analysis was done on a specimen that had been dried *in vacuo* at 80° C. (loss, 8.09%). Found: C, 75.13; H, 6.66; N, 5.08; OMe, 9.16%. Calc. for  $C_{20}H_{21}O_3N$ : C, 74.30; H, 6.50; N, 4.63; 1 OMe, 9.60%.

#### *l*-Corypalmine

The combined fractions (BCE and EEC) when left in contact with methanol yielded about 0.1 gm. of crystalline base, which, when recrystallized from chloroform-methanol melted in an evacuated tube at 246° C. In admixture with a specimen of *l*-corypalmine melting *in vacuo* at 244° C. it melted at 245 to 246° C. A small portion was methylated with diazomethane. The resulting non-phenolic base when recrystallized from ether melted at 141° C., and in admixture with a specimen of *l*-tetrahydro-palmatine it melted at the same temperature.

The mother liquor from which no more *l*-corypalmine could be crystallized was neutralized with hydrogen bromide and the base regenerated from the sparingly soluble salt that separated. It could not be crystallized and was therefore methylated with diazomethane. The resulting non-phenolic base was recrystallized from methanol, and it then melted at 163° C. It did not seem to be identical with any base in the author's possession. Found: C, 71.04; H, 6.34; N, 4.06, 3.94; OMe, 19.35%. Calc. for  $C_{20}H_{21}O_4N$ : C, 70.80; H, 6.20; N, 4.13; 2 OMe, 18.29%.

#### Fraction BSE

The precipitate (BSE) was redissolved in dilute hydrochloric acid and the filtered solution basified with ammonia and extracted with a large volume of ether. The washed ether solution was evaporated but the resin thus obtained could not be crystallized. A small portion was methylated with diazomethane and the non-phenolic product converted to hydrobromide. The base, regenerated from the sparingly soluble hydrobromide, was recrystallized from ether-hexane, and it then melted at 92° C. either alone or in admixture with alkaloid F60 obtained directly from fraction (BS).

The main fraction of (BSE) was converted into hydrobromide in methanol-acetone and the salt that separated was washed with the same solvents. The free base was regenerated but could not be crystallized. It was methylated with diazomethane and the non-phenolic product recrystallized from ether and from methanol. It then melted at 167° C. In admixture with the base (m.p. 163° C.) similarly obtained from (BCE) it was completely liquid at 150° C. although the analytical figures indicate the same formula. Found: C, 70.94; H, 6.21; N, 3.94; OMe, 17.72%. Calc. for  $C_{20}H_{21}O_4N$ : C, 70.80; H, 6.20; N, 4.13; 2 OMe, 18.30%.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS  
XXXVII. *DACTYLICAPNOS MACROCAPNOS* HUTCHINSON<sup>1</sup>

BY RICHARD H. F. MANSKE<sup>2</sup>

Abstract

*Dactylicapnos macrocapnos* Hutchinson is the first plant of the genus *Dactylicapnos* Wall. that has been chemically examined. Only three known alkaloids were found, namely, protopine, allocryptopine, and stylopine. Phenolic alkaloids were absent.

The genus *Dactylicapnos* Wall. contains about eight species native to China and the Himalayan regions. Some botanists regard it as synonymous with *Dicentra*, but the climbing habit of the plants alone is sufficient to warrant at least some distinction. Whether or not such a distinction is justified on chemical grounds is not yet clear. The number of Asiatic *Dicentra* species that have been chemically investigated is too small to permit of significant speculation as to their relationship to *Dactylicapnos* species. At all events only one species of the latter, namely, *D. macrocapnos* Hutchinson, has been examined and the results are recorded herewith.

Only three alkaloids, namely, protopine, allocryptopine, and stylopine, were present. No significant quantities of phenolic bases could be found, and the total uncrystallized residue consisted of a very small portion only of the total alkaloids.

Some of the plant for this investigation was kindly supplied by Dr. R. R. Stewart, Gordon College, Rawalpindi, India. It was collected in the District of Naini Tal, India, at an altitude of 7000 ft. The remainder of the material was grown in a local garden from seeds kindly sent by Dr. Stewart, to whom the author is sincerely grateful.

Experimental

There was available a total of 9540 gm. of dried and ground material of which the roots constituted 630 gm. The latter were extracted separately and the extracts were combined, since no significant amount of material crystallized directly from either extract. The procedure for isolating the various fractions was that repeatedly used by the writer in these investigations (1).

*Protopine*

The fraction (BS) was redissolved in dilute hydrochloric acid, the filtered solution basified with ammonia, and extracted with ether. The residue from the washed extract deposited 3 gm. of protopine when dissolved in a little methanol. When recrystallized from chloroform-methanol it melted sharply

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<sup>2</sup> Chemist.

at 211° C.\* either alone or in admixture with an authentic specimen of protopine.

#### *Allocryptopine*

The methanolic filtrate from the protopine was redissolved in dilute hydrochloric acid and the remaining protopine largely precipitated as the sparingly soluble nitrate by adding an excess of potassium nitrate. The base remaining in solution was reprecipitated with ammonia and extracted with ether. The resinous base obtained from the washed extract crystallized readily in contact with methanol and after washing and drying melted sharply at 160° C., either alone or in admixture with allocryptopine. The yield was about 2.1 gm.

#### *Stylopine*

The fraction (BC) was redissolved in hot dilute hydrochloric acid. On cooling, a sparingly soluble hydrochloride separated. The free base was regenerated from the latter and recrystallized from chloroform-methanol. It then melted at 206° C. and this melting point was not depressed when the base was mixed with a partly racemic specimen of stylopine from *Corydalis nobilis* (2). The optical activity  $[\alpha]_D^{24} - 112^\circ$  ( $c = 0.4$  in chloroform) indicated that this base was *l* + *dl*-stylopine. A small portion was racemized by oxidation and subsequent reduction. It then melted sharply at 221° C. The total yield was 0.9 gm. The mother liquors from the stylopine on exhaustive examination yielded only a little more of the same base, together with small amounts of protopine and allocryptopine.

The plant contained a considerable quantity of fumaric acid.

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\* All melting points are corrected.

# ON THE SYNTHESIS OF OPTICALLY ACTIVE $\beta$ -PHOSPHATIDIC ACIDS<sup>1</sup>

BY ERICH BAER<sup>2</sup>, IRA B. CUSHING<sup>3</sup>, AND HERMANN O. L. FISCHER<sup>4</sup>

## Abstract

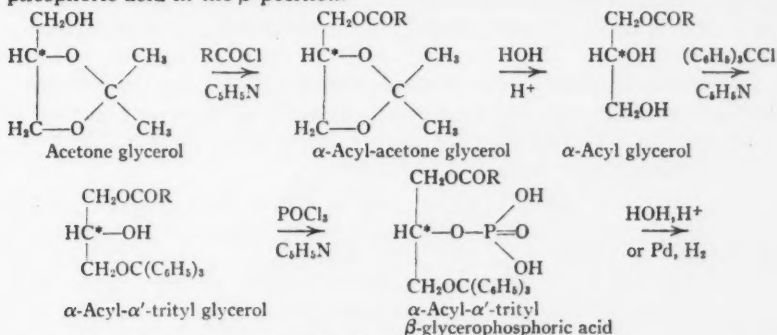
A method is outlined for the synthesis of one series of optically active  $\beta$ -phosphatidic acids from *d*(+)-acetone glycerol. The syntheses of the following new compounds are described: *l*(-)- $\alpha$ -benzoyl glycerol,  $\alpha'$ -trityl *l*- $\alpha$ -benzoyl glycerol, potassium  $\alpha'$ -trityl- $\alpha$ -benzoyl  $\beta$ -glycerophosphate (active and racemic), and potassium  $\alpha$ -benzoyl  $\beta$ -glycerophosphate (racemic).

## Introduction

Methods for the synthesis of optically active glycerol derivatives have been developed in this laboratory (1) and have led to the synthesis of  $\alpha$ -mono-glycerides (2), diglycerides (6), triglycerides (2), and glycerol ethers (5).

Unsubstituted  $\alpha$ -glycerophosphoric acids of both the *d*- and *l*-configuration have likewise been synthesized. The configurative relationship of all these aforementioned compounds to the *d*- and *l*-glyceraldehyde is established by the method of synthesis.

The enzymatic hydrolyses of *l*(-)- $\alpha$ -glycerophosphate (3), *d*(+)- $\alpha$ -glycerophosphate, and *d,l*- $\alpha$ -glycerophosphate have been investigated (4). It seemed that the synthesis of optically active  $\beta$ -phosphatidic acids would be of value both to provide suitable substrates for further enzyme experiments and to provide intermediates for the synthesis of optically active lecithins. Because  $\beta$ -lecithins predominate in many natural sources, attention was now directed to the synthesis of the enantiomorphic forms of phosphatidic acids with phosphoric acid in the  $\beta$ -position.



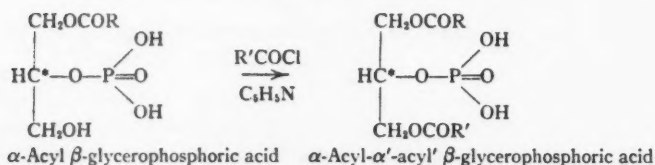
<sup>1</sup> Manuscript received January 25, 1943.

Contribution from the Department of Chemistry, Banting Institute, University of Toronto, Toronto, Ont., based on a thesis submitted by I. B. Cushing to the Graduate School of the University of Toronto in partial fulfilment of the requirements for the degree of Doctor of Philosophy, February, 1942.

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<sup>4</sup> Research Professor of Organic Chemistry, University of Toronto.



The synthesis was carried out in the following steps:  $\alpha'$ ,  $\beta$ -acetone glycerol  $\rightarrow$   $\alpha$ -acyl- $\alpha'$ ,  $\beta$ -acetone glycerol  $\rightarrow$   $\alpha$ -acyl glycerol  $\rightarrow$   $\alpha'$ -trityl- $\alpha$ -acyl glycerol  $\rightarrow$   $\alpha'$ -trityl- $\alpha$ -acyl  $\beta$ -glycerophosphoric acid  $\rightarrow$   $\alpha$ -acyl  $\beta$ -glycerophosphoric acid  $\rightarrow$   $\alpha$ -acyl- $\alpha'$ -acyl'  $\beta$ -glycerophosphoric acid. In preliminary work, benzoic acid provided the acyl group first introduced. The last step has not yet been tried. Each step was carried out first with racemic material, and later, by the same methods, with the optically active compounds.

This paper constitutes only an interim report of some experiments, published now because it has been necessary to discontinue this phase of the work temporarily. It is intended to continue the experiments at a later date with fatty acids in place of the aromatic acids.

With regard to the experimental details, some introductory remarks are given:

The preparation of optically active benzoyl acetone glycerol has been reported in an earlier paper (1).

Its acid hydrolysis with 0.5 *N* sulphuric acid\* or dilute acetic acid gave rise to the formation of *l*(-)-monobenzoyl glycerol, which has not been previously described.

A subsequent tritylation of the racemic  $\alpha$ -monobenzoyl glycerol and the *l*(-)-monobenzoyl glycerol yielded the corresponding  $\alpha'$ -trityl- $\alpha$ -benzoyl glycerols.

With both  $\alpha$ -positions thus blocked, phosphoric acid was then introduced in the  $\beta$ -position by the well known method employing phosphorus oxychloride and pyridine. The best results were secured when the reaction time of phosphorylation was limited to ten minutes.

The removal of the trityl group could be accomplished either by catalytic reduction at room temperature with hydrogen and palladium in water solution or by acid hydrolysis [e.g., with *N*/10 hydrochloric acid (40 min.) or 60% acetic acid (14 hr.)]. Only an approximate value of the rotation of the potassium salt of  $\alpha$ -benzoyl  $\beta$ -glycerophosphoric acid can be reported at this time.

### Experimental

#### *l*(-)- $\alpha$ -Benzoyl Glycerol

A mixture of 22.6 gm. of *d*(+) benzoyl acetone glycerol ( $[\alpha]_D = +13.5^\circ$ ), 130 cc. of water, and 23 cc. of glacial acetic acid was warmed to  $80^\circ\text{C}$ . and stirred vigorously for 20 min. At the end of this time a sharp change in

\* See Hibbert and Hallonquist (*Can. J. Research*, 8: 129-136, 1933.) for an improvement on the method of Fischer, Bergmann, and Bärwind (*Ber.* 53: 1589-1605, 1920.).

appearance from an opalescent to a clear solution indicated the completion of hydrolysis. The water and acetic acid were removed by vacuum distillation (at 10 mm. and 40°) and the residual syrup was poured into an evaporating dish. When placed *in vacuo* over sulphuric acid, the syrup solidified within 15 min. to a crystalline product weighing 18.8 gm. This material, crystallized from a solution containing 70 cc. of carbon tetrachloride and 10 cc. of chloroform, gave 14.4 gm. (76%) of the benzoate; m.p. 66.5 to 67°.\* The melting point was not raised by further recrystallizations. Optical rotations:  $[\alpha]_D = -16.8^\circ$  [ $c = 10.53$  in dry ethanol];  $[\alpha]_D = -15.3^\circ$  [ $c = 10.91$  in dry pyridine]. Calc. for  $C_{10}H_{12}O_4$  (196.1): C, 61.21; H, 6.17%. Found: C, 60.89, 60.86; H, 5.88, 6.01%.

$\alpha'$ -Trityl- $\alpha$ -benzoyl Glycerol†

To 5 gm. of racemic  $\alpha$ -benzoyl glycerol were added 10 cc. of dry quinoline and 7.1 gm. of trityl chloride. The mixture, adequately protected against moisture, was warmed for one hour on a boiling water-bath and was then allowed to stand overnight at room temperature. The clear viscous solution was taken up in 200 cc. of ether and 50 cc. of water. The ether layer was washed in rapid succession with two 100 cc. portions of 0.5 *N* sulphuric acid, 50 cc. of water and finally with 50 cc. of 1% sodium bicarbonate. The ether solution was dried with anhydrous sodium sulphate, concentrated to 50 cc., and set aside for 24 hr. at room temperature. The substance separated in well formed crystals. Yield, 60%; m.p. 124 to 125°. For recrystallization the crystals were redissolved in 250 cc. of boiling, dry, and alcohol-free ether, and the solution was concentrated to a volume of 50 cc. The melting point of the new crystalline material was 125 to 126.5°, and it could not be raised by further recrystallization. Calc. for  $C_{25}H_{26}O_4$  (438.5): C, 79.4; H, 5.97%. Found: C, 78.88; H, 6.05%.

$\alpha'$ -Trityl *l*- $\alpha$ -Benzoyl Glycerol

The active compound is prepared in virtually the same way as the inactive, using *l*(-)- $\alpha$ -benzoyl glycerol as starting material. The only difference was the use of water instead of sulphuric acid for the removal of the pyridine from the ether solution. This change in procedure yielded an end-product of greater purity. The residue left after evaporation of the ether solution was dried for a week over sulphuric acid *in vacuo*. The syrup was taken up in boiling ether, and petroleum ether (80 to 100° C.) was added to the point of incipient turbidity. After 12 hr. at room temperature a mass of fine needles filled the flask. These were filtered off, washed with dry ether, and dried. After one recrystallization a yield of 40% of trityl ether was obtained; m.p. 89 to 90. Optical rotations: (i)  $[\alpha]_D = -22.1^\circ$  [ $c = 10.16$  in dry pyridine]; (ii)  $[\alpha]_D = -12.6^\circ$  [ $c = 10.01$  in dry ethanol]; (iii)  $[\alpha]_D = -11.5^\circ$  [ $c = 9.99$

\* Melting points are uncorrected.

†  $\alpha'$ -Trityl- $\alpha$ -benzoyl glycerol has been described by Verkade, Cohen, and Kroege (*Rec. trav. chim.* 59: 1123-1140. 1940). Since their paper is not available in the original at present, we are giving the preparation of the compound explicitly.



in dry benzene]. Calc. for  $C_{29}H_{28}O_4$  (438.5): C, 79.4; H, 5.97%. Found: C, 79.49; H, 6.08%.

*Potassium  $\alpha'$ -Trityl- $\alpha$ -benzoyl  $\beta$ -Glycerophosphate*

A solution of 2 gm. of  $\alpha'$ -trityl- $\alpha$ -benzoyl glycerol in 3 cc. of dry pyridine was strongly cooled (dry ice and acetone) and 0.45 cc. of phosphorus oxychloride (theor. 0.42 cc. or 0.70 gm.) was quickly introduced from a pipette. As the flask warmed to room temperature it was rotated to mix the reactants. Crystals of pyridine hydrochloride appeared in about two minutes. Ten minutes after the addition of phosphorus oxychloride, the flask was again strongly cooled, and 9 cc. of pyridine and 50 cc. of water were added. The solution was poured on to 20 gm. of ice. The mixture was vigorously stirred, and 165 cc. (approx. 10% excess) of 1.0 *N* hydrochloric acid was added rapidly. The fine granular precipitate was quickly filtered off with suction and washed with 50 cc. of water. The precipitate was dried sufficiently to permit its easy separation from the filter paper. Whenever hydrochloric acid was omitted in the above step of the procedure, a non-crystalline potassium salt was obtained.

The pyridine salt was triturated with 1.0 gm. of potassium carbonate in a heavy-walled 40 cc. centrifuge tube under 10 cc. of alcohol-free ether. Bubbles of carbon dioxide were rapidly evolved. Whenever the precipitate had inadvertently been allowed to become too dry for rapid reaction with carbonate, a few drops of water were added. At this stage the product was usually a mealy mass, but if a little more water was present the product was syrupy. The ether was decanted and the product was dried *in vacuo* over sulphuric acid for 12 hr. at room temperature. Its solution in 40 cc. of acetone was centrifuged, the supernatant liquid was warmed to the boiling point, and 0.75 cc. of water was added. The crystals obtained on slow cooling were filtered off and dried *in vacuo*, first at room temperature over sulphuric acid, and then for two hours at 100° C. over phosphorus pentoxide. The yield was 1.80 gm. (67%). Calc. for  $C_{29}H_{28}O_7PK_2$  (594.66): P, 5.22; ash, 29.33%. Found: P, 5.30, 5.38; ash, 29.38, 29.08%.

To obtain a fairly reproducible value of the melting point (174 to 175° C.), it was necessary to introduce the sample into a bath already heated to within 30° of the melting point and then to heat the bath at the rate of 10° per minute.

*Potassium  $\alpha'$ -Trityl l- $\alpha$ -Benzoyl  $\beta$ -Glycerophosphate*

The trityl ether of l(-)- $\alpha$ -benzoyl glycerol was phosphorylated as has been described for the corresponding racemic compound. The yields of the potassium salt varied from 56 to 70%; m.p. 174 to 175° C. Calc. for  $C_{29}H_{28}O_7PK_2$ : P, 5.22; ash, 29.33%. Found: P, 5.20, 5.32; ash, 29.46%.

*Potassium  $\alpha$ -Benzoyl  $\beta$ -Glycerophosphate*

(A) Reductive Detritylation

A quarter gram of palladium chloride was dissolved in water, and to the solution was added the equivalent amount of 1 *N* sodium hydroxide solution.



TABLE I  
OPTICAL ROTATIONS

Solvent	Concentration	$[\alpha]_D$
Water	8.5	-15.6°
50% Methanol 50% Water (by volume)	10.02	-14.2°
Dry acetone	5.91	- 8.8°
Dry pyridine	7.53	- 5.0°
2 cc. Pyridine + 1 drop water	7.5	- 7.5°
Dry dioxane	7.91	- 4.0°

The precipitated hydroxide was coagulated by boiling, separated by centrifugation, and washed with distilled water in the centrifuge tube until the wash water was neutral to litmus.

The palladium hydroxide was washed into the reaction chamber with 20 cc. of distilled water, and shaken in the presence of pure hydrogen until the resulting finely divided palladium black ceased to absorb hydrogen. Half a gram of racemic potassium benzoyl trityl glycerophosphate was then added, and the reduction carried out with hydrogen under a pressure of a 50 cm. water column. The absorption of hydrogen proceeded slowly and ceased after seven hours, when almost the theoretical amount of hydrogen had been absorbed (21 cc. at N.T.P.). The opalescent solution was extracted with ether. (On evaporation of the ether, 0.21 gm. of triphenylmethane was obtained; m.p. 92 to 93°.) The aqueous solution was freed from palladium and evaporated *in vacuo* at a bath temperature of 35°. The residue was taken up in 20 cc. of methanol and 2 cc. of water. To the centrifuged solution, still slightly cloudy with palladium, was added 50 cc. of acetone. The precipitate, a fine white powder, weighed 0.26 gm. (87%). A reprecipitation sufficed to remove the rest of the palladium. When heated in a melting point tube, the salt darkened gradually without melting. Calc. for  $C_{10}H_{13}O_7PK_2$  (354.4): P, 8.81%. Found: P, 8.84, 8.87%.

(B) Detritylation by Hydrochloric Acid

One gram of potassium salt was dissolved in 10 cc. of water and 4.88 cc. of 1 *N* hydrochloric acid was added. This was sufficient to give a solution tenth normal in free hydrochloric acid after formation of potassium chloride. A gelatinous precipitate of benzoyl trityl glycerophosphoric acid was formed at once. The mixture was shaken vigorously for 35 min. to break up the gelatinous mass as detritylation proceeded. The end of detritylation was clearly marked by the change in the character of the precipitate from gelatinous to crystalline. The tritanol was filtered off and washed with 10 cc. of water.

It weighed 0.44 gm. (theor. 0.437 gm.). To the filtrate was added 1.50 cc. of 1 *N* potassium hydroxide, sufficient to neutralize all free hydrochloric acid, and the solution was evaporated to dryness *in vacuo* at a bath temperature of 40° C. The dry residue was extracted with 50 cc. of acetone and the filtered extract was evaporated to dryness *in vacuo*. The clear syrup was taken up in 15 cc. of methanol, a few drops of phenolphthalein solution were added, and the solution was titrated with a 1 *N* solution of potassium hydroxide in methanol to the first trace of pink colour. The addition of 25 cc. of acetone to the clear methanol solution precipitated 0.51 gm. (87%) of the potassium salt of  $\alpha$ -benzoyl  $\beta$ -glycerophosphoric acid as a fine white powder. Calc. for  $C_{10}H_{13}O_7PK_2$  (354.4): P, 8.79; ash, 49.6%. Found: P, 8.80, 8.96; ash, 49.3%.

*Potassium l- $\alpha$ -Benzoyl  $\beta$ -Glycerophosphate*

Insufficient work has been done on the detritylation of the optically active compound. The only optical rotation of the potassium salt of  $\alpha$ -benzoyl  $\beta$ -glycerophosphoric acid that was observed was found to be approximately  $[\alpha]_D = +9^\circ$  (in water).

**Acknowledgments**

Thanks are due to the National Research Council of Canada for student-ships awarded to one of the writers (I. C.) for the years 1938-39 and 1939-40, and also to the Banting Research Foundation for a grant for the year 1940-41.

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## CATHODE SURFACE CHANGES IN THE PRESENCE OF GELATIN DURING ELECTRODEPOSITION OF COPPER<sup>1</sup>

BY W. GAUVIN<sup>2</sup> AND C. A. WINKLER<sup>3</sup>

### Abstract

Measurements of the cathode polarization during electrodeposition of copper from acid copper sulphate solutions indicate that introduction of gelatin into the electrolyte decreases the area of the cathode available for deposition, or active area, owing to adsorption of gelatin on the active centres. This decrease in area causes an increase in the true current density, with a resulting increase in cathode polarization, the former being assumed the main factor in causing an increase in the rate of nuclear formation and decrease in grain size.

### Introduction

It was shown in a previous paper (2) that the cathode polarization at different specimens of copper cathodes, polished in the same way, changed with time in a manner that differed with different specimens. It was found, however, that under closely controlled conditions of electrolysis, the polarization eventually assumed a constant or steady state value.

In the course of determining whether the same steady state value of the polarization would be attained under given conditions of electrolysis, regardless of the initial condition of the cathode surface, an experiment was made in which a very finely crystalline surface was imparted to the cathode by electrolyzing to constant polarization in an electrolyte to which gelatin had been added. It was expected, in conformity with the behaviour shown in other experiments, that using such a cathode, and electrolyzing under conditions that normally led to a more coarsely crystalline surface, would result in a gradual increase in polarization to the equilibrium value. However, a decrease, not an increase, in polarization was in fact observed. This observation prompted a more detailed study of the behaviour, the results of which are presented in this paper.

### Experimental

The apparatus and technique employed were similar, in all respects, to those used in previous investigations (2, 3).

Prior to each experiment, the desired surface was imparted to the cathode by electrolyzing in appropriate electrolyte under controlled conditions of apparent current density and temperature, until constant polarization was reached. When the desired surface was thus obtained, the electrolyte used in plating this cathode specimen was replaced by the new solution investigated, and the cathode polarization determined as a function of time at a constant apparent current density.

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

<sup>2</sup> Postgraduate Student, holder of International Nickel Co. (Inco) Scholarship.

<sup>3</sup> Assistant Professor of Chemistry.

### Results

Experiments were first made using cathodes to which definite surface characteristics were imparted by electrolyzing to constant polarization, with gelatin in the electrolyte.

Two cathode types were prepared, using electrolytes containing 10 mg. per litre of gelatin (solution No. 20, see Table I, given in reference (3)) and 750 mg. per litre of gelatin (solution No. 23), respectively. The first was obtained at an apparent current density of 4.2 amp. per dm.<sup>2</sup>, and the other at 4 amp. per dm.<sup>2</sup>. A third specimen was prepared, using an electrolyte of higher acidity, but containing only 2 mg. per litre of gelatin (solution No. 37), at an apparent current density of 2 amp. per dm.<sup>2</sup>. These three different treatments gave cathodes with quite finely crystalline surfaces. No difference could be detected between the first two, when examined under the microscope with  $\times 50$  magnification, but both appeared somewhat finer than the third, obtained with the lower gelatin concentration.

The cathodes so prepared were then used during electrolysis at 26.4° C. with an apparent current density of 2 amp. per dm.<sup>2</sup>, in the standard electrolyte (solution No. 17), containing 125 gm. per litre of copper sulphate pentahydrate, 150 gm. per litre of sulphuric acid, but no gelatin.

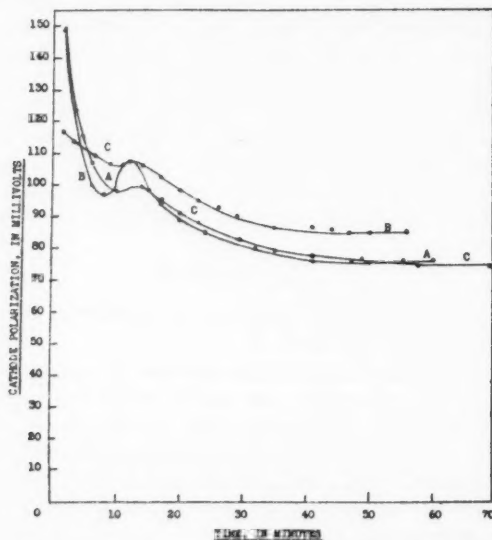


FIG. 1. Effect of gelatin on cathode surface. Solution: No. 17. Apparent current density: 2 amp. per dm.<sup>2</sup>. For Curve A:— Temperature: 26.4° C. Initial surface: that obtained in solution No. 20 (10 mg. per litre of gelatin) at 4.2 amp. per dm.<sup>2</sup>. For Curve B:— Temperature: 25.3° C. Initial surface: that obtained in solution No. 23 (750 mg. per litre of gelatin) at 4 amp. per dm.<sup>2</sup>. For Curve C:— Temperature: 26.4° C. Initial surface: that obtained in solution No. 37 (2 mg. per litre of gelatin) at 2 amp. per dm.<sup>2</sup>.

Data for the change in cathode polarization with time for the three surfaces are plotted in Fig. 1, Curves A, B, and C, respectively. Two points of experimental interest may be noted: a slight increase, followed by a decrease in cathode polarization after approximately 12 min. from the beginning of electrolysis, a behaviour that has already been reported (2). Also, taking into account small differences in the temperatures at which the experiments were made, the steady state polarization values eventually attained a value that is essentially the same as the steady state values previously recorded for electrolysis from the standard electrolyte under similar conditions of apparent current density and temperature. The final surfaces had the same coarsely grained characteristics of the standard base previously obtained. However, the courses of the curves in attaining the steady state polarization were completely unexpected, and confirmation was sought by varying the experimental details. An experiment was made in which the cathode was first given a relatively fine crystalline surface by electrolyzing at an apparent current density of 2 amp. per dm.<sup>2</sup> and temperature of 26.4° C. to constant polarization in an electrolyte containing 2 mg. per litre of gelatin (solution No. 37). This fine surface was then used as the cathode in electrolysis to constant polarization in the standard electrolyte (solution No. 17), under the same conditions. The change of cathode polarization with time during the latter electrolysis is plotted in Fig. 2, Curve A. Again, the cathode polarization decreased with time, while visual observations easily revealed

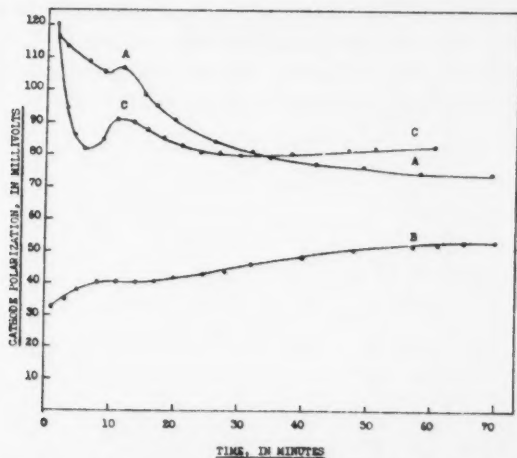


FIG. 2. Effect of gelatin on cathode surface. Temperature: 26.4° C. For Curve A:—Solution: No. 17. Current density: 2 amp. per dm.<sup>2</sup>. Initial surface: that obtained after 62 min. deposition from solution No. 37 (2 mg. per litre of gelatin) at an apparent current density of 2 amp. per dm.<sup>2</sup>. For Curve B:—Solution: No. 28 (10 mg. per litre of gelatin). Apparent current density: 0.5 amp. per dm.<sup>2</sup>. Initial surface: Standard base (obtained at the end of Curve A). For Curve C:—Solution: No. 17. Apparent current density: 2 amp. per dm.<sup>2</sup>. Initial surface: that obtained at the end of Curve B, above.

that the surface of the cathode had become considerably more coarsely crystalline and had acquired the surface characteristics of the standard base.

The electrolyte was then changed to one containing 10 mg. per litre of gelatin (solution No. 28) and electrolysis resumed at an apparent current density of 0.5 amp. per dm.<sup>2</sup>, until steady state polarization was again reached. The cathode polarization now showed a marked increase with time, as indicated by Curve B, Fig. 2. Inspection showed that surface condition had changed from the coarsely crystalline structure of the standard base to a finer-grained surface.

The solution was then changed back to the standard electrolyte No. 17, containing no gelatin, and electrolysis continued at an apparent current density of 2 amp. per dm.<sup>2</sup>, until constant polarization values were again obtained. The polarization again decreased with time (Curve C, Fig. 2), attaining essentially the steady state value generally found for electrolysis under standard conditions, and again the surface had changed to the more coarsely crystalline condition of the standard base.

Further information was obtained by working with solutions containing various amounts of gelatin. The surface of a cathode was conditioned by electrolyzing at an apparent current density of 2 amp. per dm.<sup>2</sup> until constant polarization was attained, using an electrolyte containing 1 mg. per litre of gelatin (solution No. 26). On this visibly fine-grained surface, a deposit appearing even finer to the naked eye was obtained, using the same apparent current density, but with an electrolyte now containing 5 mg. per litre of gelatin (solution No. 27). The increase of cathode polarization with time during deposition of this finer deposit is shown in Fig. 3, Curve A. The gelatin

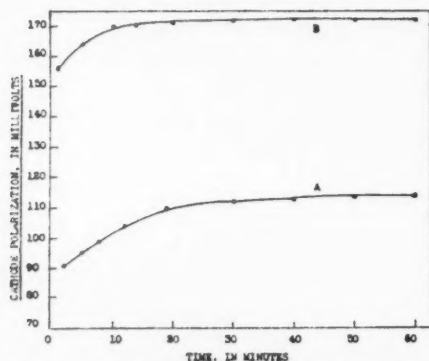


FIG. 3. Effect of gelatin on cathode surface. Temperature: 25° C. Apparent current density: 2 amp. per dm.<sup>2</sup> For Curve A:— Solution: No. 27 (5 mg. per litre of gelatin). Initial surface: that obtained after 60 min. deposition from solution No. 26 (1 mg. per litre of gelatin) under similar conditions. For Curve B:— Solution: No. 28 (10 mg. per litre of gelatin). Initial surface: that obtained at the end of Curve A, above.

content of the electrolyte was increased further to 10 mg. per litre (solution No. 28), other conditions remaining the same, and the cathode polarization increased with time, in accordance with Curve B, of Fig. 3. No change in fineness of surface structure was apparent at  $\times 50$  magnification, following the last electrolysis.

Having observed the manner in which the presence of gelatin influenced the shape of the polarization-time curves under various conditions, it was of interest to determine how the behaviour might be reflected in the relation between cathode polarization and current density. The procedure for establishing this relation has been dealt with previously (2, 3). One cathode was brought to standard surface condition, by electrolysis at an apparent current density of 2 amp. per dm.<sup>2</sup> in the standard electrolyte (solution No. 17), until steady state polarization was reached. A second cathode was given different, but again definite surface characteristics by electrolysis to constant polarization at the same current density, using an electrolyte containing 2 mg. per litre of gelatin (solution No. 37), the final surface having assumed a fine crystalline structure. The relation between cathode polarization and apparent current density was then established for each cathode in the standard electrolyte, under standard conditions. The results are shown in Fig. 4, Curve A

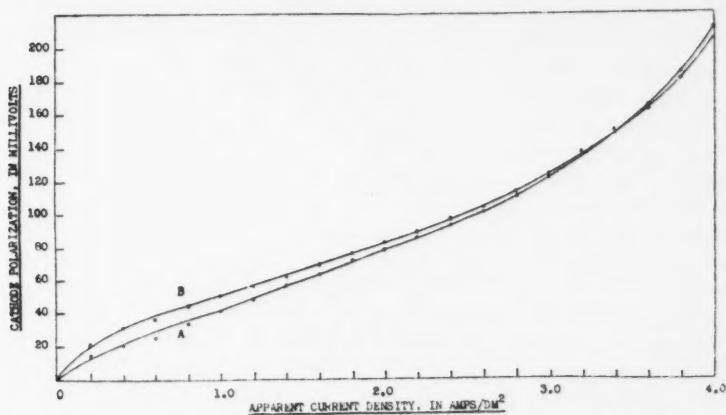


FIG. 4. Temperature: 25° C. Initial surface: for A, standard base; for B, different base. Solution: No. 17 (for both curves).

representing the cathode-polarization-apparent-current-density curve, using the standard base as initial surface, and Curve B, using the much finer-grained cathode as the initial surface. The interesting feature of the two curves is that the cathode polarization is somewhat higher at lower current densities when deposition takes place on the surface laid down initially in the presence of gelatin, in spite of the fact that this surface was finer than the other. At higher current densities, the discrepancies disappear.



### Discussion

It was shown in a previous paper (2) that at a given apparent current density, in the absence of addition agent, a decrease in crystal size caused a decrease in cathode polarization values. This behaviour was logically attributed to an increase in the true area of the cathode, with a consequent decrease of the true current density at which deposition was actually taking place. However, the present experiments, made with electrolytes containing gelatin, show exactly the opposite effect, whether the decrease in grain size was from a coarsely crystalline surface to a fine one (Fig. 2, Curve *B*), or from a fine-grained surface to a still finer-grained one (Fig. 3, Curves *A* and *B*). The opposite change in surface, from a finely crystalline structure to a coarsely grained one, normally accompanied by an increase in cathode polarization, actually resulted in a decrease in polarization in the presence of gelatin (Fig. 1, Fig. 2, Curves *A* and *C*). It is evident, therefore, that since a fine structure is always associated with a large true area (2), gelatin must be able to impart to such a fine-grained surface the characteristics normally associated with a coarser surface of smaller true area. The only explanation that can be advanced to reconcile the results obtained is that not all of the surface is active during deposition but only a certain fraction of it, which may be called the "active surface", and which is susceptible of being decreased by gelatin. It may be noted that Volmer, in 1931 (1), showed that deposition always starts from crystal corners, although it may sometimes start from an edge, but never from a crystal face. He called these corners "active centers".

From previous results (2), it may be said that, in the absence of gelatin, the active area increases with the true area; this is logical in view of the greater number of these active centres present in a finer-grained deposit. From the results obtained in the present investigation, however, it is obvious that, although gelatin increases the true area, the active area is considerably reduced. This will result in an increase in the true current density, accompanied by an increase in cathode polarization. Since an increase in current density is always accompanied by an increased rate of nuclear formation (5, 7), the large increase in current density caused by the reduction in active area in the presence of gelatin greatly increases the nuclear formation and will cause a decrease in the crystal size, i.e., result in a finer structure. The relation existing between cathode polarization and true current density is not affected by the new concept, but the true current density is now determined, not by the true area, but by the active area.

Reduction of the active area of a deposit by gelatin is probably best explained by adsorption. Since deposition has been shown to begin at corners, and adsorption, whether "chemisorption", "van der Waals", or purely electrostatic, will logically be greater at these points, it is seen that adsorption of gelatin on these active centres will prevent further deposition of copper, and will cause a large reduction in the active area. This explanation accounts for the very small amount of gelatin needed to exert a beneficial action on the deposit. As little as a fraction of a milligram per litre radically changes



the appearance of the deposit. A large amount, on the other hand, should, according to these views, so reduce the active area, or area available for deposition, that the large number of nuclei formed are allowed to grow only to a very small extent before gelatin covers the active centres, and the presence of gelatin on almost all the available active centres by which the new crystals first develop should considerably reduce the adherence, resulting finally in a powdery deposit. It is known, in fact, that a large amount of gelatin is conducive to formation of a powdery deposit.

The assumption that adsorption is responsible for the reduction in active area of a deposit gains considerable support from the observation, reported in an earlier paper (3), that the relative increase in cathode polarization due to the presence of a given amount of gelatin is considerably greater at lower temperatures, where adsorption is greater. Similarly, the fact that adsorption of gelatin tends towards a maximum for given conditions of electrolysis (4, 6) is also paralleled by a similar observation for the cathode polarization. This would account for the fact that the reduction in active area, resulting in an increased fineness of the deposit, at first very rapid for small gelatin concentrations, decreases less rapidly with increased amount of the addition agent, making the visual appraisal of the degree of fineness of a deposit difficult for the higher concentrations of gelatin. This is substantiated by the visual observations reported for experiments described in Figs. 1 and 3, and also, in a qualitative manner at least, by the fact that Curves *A* and *B*, of Fig. 1, obtained on surfaces deposited in solutions containing 10 and 750 mg. per litre of gelatin, respectively, exhibited much larger initial cathode polarization for the same current density than Curve *C*, obtained on a surface deposited from a solution containing only 2 mg. per litre of gelatin. The larger cathode polarization, implying larger true current density for a given current, associated with smaller active area, shows that the surface laid down in an electrolyte containing 2 mg. per litre of gelatin had a larger area (i.e., was coarser-grained) than the other two electrodes, with surfaces characteristic of electrolytes containing higher concentrations of gelatin.

It is interesting to note that the suggestions made here do not assume any fundamental change in any of the deposition processes, the only change being, in fact, an increase in the true current density in the presence of the gelatin. A confirmation of the fact that no radical change in the deposition process takes place in the presence of gelatin is very well shown by the fact that all cathode polarization curves obtained under widely different conditions conform within a range of current density to the same general equation, this fact being true whether the solution does, or does not, contain gelatin (3).

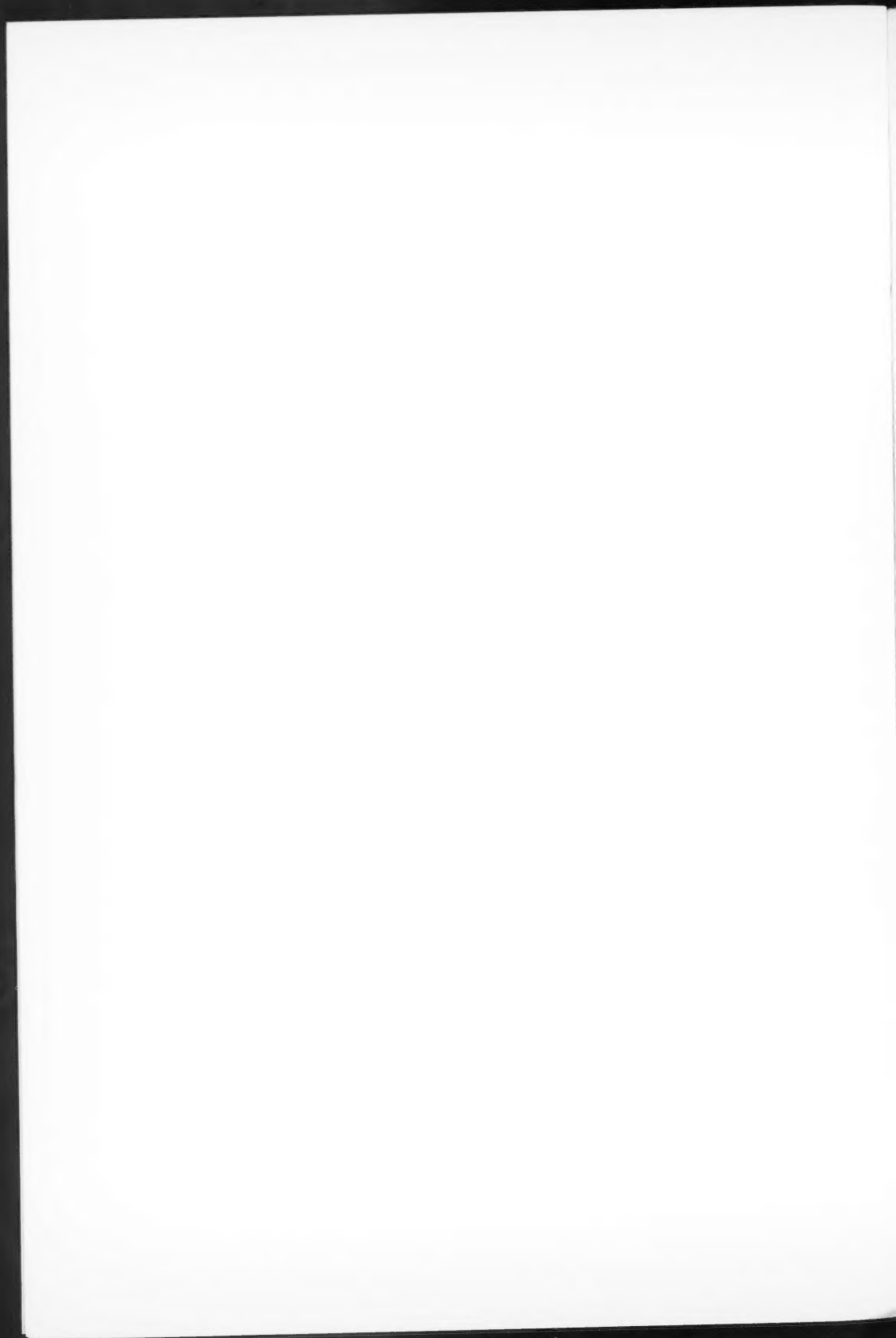
The results depicted in Fig. 4 show that cathode polarization values obtained, using a finely crystalline base deposited from solution containing gelatin as initial surface, are appreciably greater at low current densities than those obtained on the relatively coarse standard base (obtained from solution No. 17, containing no gelatin), while they are the same for both initial surfaces at high current densities. Wood (8) showed that the influence of the base metal

disappears at higher current densities, and the results obtained are in full agreement with his findings in the upper range of the curves. The discrepancy noted at low current density can be ascribed, therefore, to the influence of the initial surfaces on which deposition was started. To explain the relative positions of the two curves, however, the concept of the active area seems to be essential. Since the active area of the initial surface, obtained in presence of gelatin, is considerably smaller than the active area of the standard base, the true current density will be greater, and will be associated with a greater cathode polarization.

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